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Scale-Up of Rapid Small-Scale Adsorption Tests to Field-Scale Adsorbers: Theoretical Basis and Experimental Results for a Constant Diffusivity

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INTRODUCTION

Recent attention about the impact of low-level contaminants on public health has encouraged a major research effort to develop effective means to identify, monitor, and remove toxic agents from drinking water, wastewater, and groundwater. Granular activated carbon (GAC) is an effective treatment technique for the removal of some toxic organics from drinking water or wastewater; however, it can be a relatively expensive process, especially if it is designed improperly. The proper design of full-scale adsorbers typically includes time-consuming and expensive pilot-scale studies.

Accordingly, a rapid method for the design of large-scale fixed-bed adsorbers from small column studies, known as the rapid small-scale column test (RSSCT), has been developed and evaluated. The three primary advantages in using the small column studies for design are: (a) a RSSCT may be conducted in a fraction of the time that is required to conduct pilot studies; (b) unlike predictive mathematical models, no isotherm or kinetic studies are required to obtain a full-scale performance prediction from a RSSCT; and, (c) a small volume of water is required to conduct the test which can be transported to a central laboratory for evaluation. Consequently, replacing a pilot study with a RSSCT would significantly reduce the time and cost of a full-scale design. The benefits of the RSSCT and the cost savings which is associated with proper design make the RSSCT a very attractive alternative to a pilot study.

In the RSSCT method, mathematical models are utilized to scale-down the full-scale adsorber to a RSSCT and maintain perfect similarity between the performance of the adsorbers. If perfect similarity is maintained, the RSSCT which utilizes a smaller adsorbent particle size than the full scale adsorber will have identical breakthrough profiles as the full-scale process. Accordingly, a number of RSSCTs could be used to evaluate the importance of

design variables such as empty bed contact time (EBCT) or bed operations such as beds in series or in parallel.

In this study, a dimensional analysis on the dispersed-flow, pore-surface- diffusion model (DFPSDM) was used to determine the scaling factors because the DFPSDM includes many of the known transport and kinetic phenomena which occur in fixed-bed adsorbers. By examining the dimensionless groups that appeared in the DFPSDM, it was found that the adsorbent particle sizes of the RSSCT and full-scale bed determined the scaling relationships between hydraulic loadings and EBCTs of the RSSCT and full-scale columns.

The scaling procedure was verified by both model calculations and experimental data. Example calculations for a RSSCT and a full-scale adsorber with the DFPSDM and the homogeneous solid diffusion model (HSDM) demonstrated that identical breakthrough profiles for single component and multicomponent systems would be obtained. These calculations proved that a RSSCT could be designed to simulate a full-scale adsorber in 1.05% of the time of a pilot-scale study. The RSSCT was verified experimentally by comparing a pilot-scale adsorber to a RSSCT. A six solute mixture with individual concentrations ranging from 3000-6000 µg/L was used. The RSSCT data were identical to the pilot data and this demonstrated experimentally that the RSSCT can be run in 4% of the time that is required for a pilot study. However, for this study it was shown that the surface diffusivity was identical for both the granular activated carbons (GACs) which were used in the RSSCT and in the full scale application.

In another study, four RSSCTs were conducted and it appeared that the surface diffusivities for the GAC which was used in RSSCTs was not identical to the surface diffusivity for the GAC which was to be used in the full scale plant. The reader should consult Berrigan[1] and Berrigan *et al.*[2,3] for a

discussion of the design considerations of a RSSCT for that situation. Berrigan[1] and Berrigan et al.[2,3] used a procedure which is modified from the one presented herein and the resulting breakthrough profiles from the RSSCT were identical to the breakthrough profiles of corresponding pilot-scale adsorbers treating the same groundwater.

EXPERIMENTAL MATERIALS AND METHODS

To experimentally evaluate the accuracy of this procedure in predicting the breakthrough profiles of a large adsorber, a RSSCT was designed to simulate the performance of a pilot-scale adsorber. The particle size for the RSSCT was selected to be as small as possible thus shortening the duration of the experiment and yet be large enough to maintain a practicable sampling schedule and avoid excessive headloss.

Apparatus and Materials.

All laboratory column experiments were conducted at 10°C, a typical groundwater temperature for the northern United States. These experiments were performed in a temperature-controlled room where maximum temperatures of 12°C were measured. All experimental equipment was constructed of glass, teflon, or stainless steel to minimize adsorption of organics.

Glass columns (Ace Glass, Inc.) of 5.0 cm and 1.1 cm diameter were used for pilot-scale and RSSCT studies, respectively. The effects of channeling and wall effects were avoided by exceeding the ratio of the particle diameter to column diameter at approximately 50.[4]

Feed solutions for the laboratory studies were prepared by mixing a concentrated aqueous solution of the volatile organic chemicals with laboratory reagent water in a headspace-free, mixing vessel prior to being fed into the column. The concentrated solution and dilution water were applied to the mixing vessel with a positive displacement metering pumps (ISCO, Inc.,

Fluid Metering, Inc.). The pH of the influent and effluent was monitored occasionally throughout the laboratory experiments was found to be 6.5. Experimental details were given by Berrigan et al.[2]

Chemicals.

All chemicals were reagent grade or better. 1,2-dibromoethane, bromoform, and chlorodibromomethane were obtained from Aldrich Chemical Co., Milwaukee, Wisconsin. Methanol, 2,2,4-trimethylpentane, chloroform and trichloroethene were obtained from Burdick and Jackson Co., Muskegon, Michigan. Tetrachloroethene and 1,1,1-trichloroethane were obtained from J.T. Baker Chemical Co., Phillipsburg, New Jersey. The GAC, Calgon's Filtrasorb-400 (Pittsburgh, PA), was used in this study. Water for influent and other solution preparation was distilled, deionized, and filtered through a Milli-Q (New Bedford, Mass.) water treatment system.

Chemical Analysis.

The volatile organic compounds (VOCs) were analyzed using a Hewlett Packard 5840 gas chromatographs which was equipped with an electron capture detector. Following the procedure which was described by Mieure (5), a liquid-liquid extraction (LLE) procedure was developed. The samples for LLE method were extracted using 5-30 ml of solution with 5-10 ml 2,2,4-trimethylpentane. 1,1,1-trichloroethane was used as the internal standard for the LLE method.

Carbon Preparation.

Representative samples of the GAC were obtained by mixing and splitting the GAC. The GAC from these samples, U.S. No. 12X40 mesh, was used in the pilot-scale work. A smaller activated carbon, 60X80 mesh, was used in RSSCT studies. The smaller carbon for the RSSCT experiments was obtained by crushing samples of the original carbon, U.S. No. 12X40, to a smaller size. The crushed carbon was sieved, retaining the U.S. No. 60X80 mesh size and

recrushed. The crushing and sieving was continued until all the carbon had passed through the 60 mesh sieve tray. The GAC which was retained on a 80 mesh sieve was then washed with Milli-Q water and dried overnight at 105°C.

APPROACH

The use of mathematical models and governing equations to define scaling relationships of the design and operational parameters between the small and full scale processes has been demonstrated by several researchers.[6-8] Beckner[9] discusses many other contributions to the subject. In summary, the following three conditions are applied to the governing equations of a system in order for the design and operation of a small-scale process to give similar operating data to that of the full scale process. First, the boundary conditions for the large and small scale processes must occur at the same dimensionless coordinate values in the dimensionless differential equations. Second, the dimensionless parameters that appear in the dimensionless differential equations for the full-scale process must equal those for the small-scale process. Finally, no change in mechanism can occur with the change in process size.

The scale-up of the RSSCT was based on the DFPSDM because it contains many of the phenomena which are known to occur in fixed-bed adsorbers[10] namely, axial dispersion, axial advective flow, surface diffusion, pore diffusion and liquid-phase mass transfer resistance. Furthermore, if exact similarity can be guaranteed for the DFPSDM, then similarity will exist for simpler models, for example, the plug-flow, pore- surface- diffusion model (PFPSDM) which ignores axial dispersion, the dispersed-flow homogeneous solid-diffusion model (DFHSDM) which lumps pore and surface diffusion together, or the plug flow homogeneous solid diffusion model (PFHSDM).

In the past, the PFHSDM has been shown to predict adsorption, desorption,

and multicomponent competition in fixed-beds.[11-16] Crittenden et al.[14] and Thacker et al.[14,15] discussed recent work in which the PFHSDM has been used to predict fixed-bed performance.

Using the DFPSDM, it is a simple matter to apply the three conditions of similarity to the model equations in dimensionless form to design a small-scale adsorber to yield similar operating data to that of the full-scale process. In the section on the DFPSDM, the model equations are presented in dimensionless form such that the boundary conditions for the large and small scale processes occur at the same dimensionless coordinate values in the DFPSDM. In the section on the development of the scaling equations, the dimensionless parameters from the model equations for the full-scale process are equated to those for the small-scale process. Accordingly, if no change in mechanism occurs with a change in process size then all three conditions will be met for similarity.

Previous Work

A small column technique has been used successfully by Beaudet et al.[18], Billelo et al.[19], and Rosene et al.[20] to determine carbon usage rates. These methods employ a fixed-bed column of fine mesh carbon and high pressure liquid chromatography (HPLC). This technique also provides qualitative information on the order of breakthrough for multicomponent mixtures. However, these investigators have not provided a method that would accurately forecast breakthrough profiles of the full scale process using their small fixed-bed results.

Frick[21] proposed a method of interpreting small-scale adsorber information with scaling equations based upon Stanton number and the solid diffusion modulus, E_d. The resulting scaling equations account for mass-transport mechanisms of solid diffusion, liquid film transfer, and advection. A small-scale experimental test could be designed from these equations to

simulate full-scale adsorber performance and provides a theoretical starting point for the work which is presented herein.

Dispersed-Flow Pore- Surface- Diffusion Model

The DFPSDM incorporates the following mechanisms: (a) advective flow, (b) axial dispersion and diffusion (This may be important when mass transfer rates are high or when low flow rates occur in the RSSCT, (c) liquid-phase mass transfer resistance, (d) local adsorption equilibrium at the exterior surface of the adsorbent, (e) surface diffusion, (f) pore diffusion and (g) competitive equilibrium of solutes upon the carbon surface (Competitive effects are assumed to be fully accounted for by multi-solute equilibrium expressions and there are no diffusion multicomponent interactions.)

For DFPSDM calculations, equilibrium isotherms equations are needed to describe multicomponent interactions. To estimate the competitive effects of solutes upon the adsorbent surface in DFPSDM calculations, ideal adsorbed solution theory (IAST)[11,15,22] was used to describe multi-solute competition. Crittenden *et al.*[23] confirmed that IAST could be used to predict competitive interactions between volatile organic chemicals (VOCs). IAST not need describe the competitive interactions in fixed-beds in order for the proposed scaling procedure to work. The only requirement is that the capacity of the GAC cannot depend on the sizes that are used in the RSSCT and the full scale process. The IAST equations are presented here only for completeness.

If the Freundlich isotherm equation is used to describe single solute behavior, IAST yields the following equation for each adsorbate:

$$\bar{C}_{p,i}(\bar{r},\bar{z},T) = \frac{\bar{Y}_i(\bar{r},\bar{z},T)Y_{e,i} - \frac{\varepsilon_p}{\rho_a}\bar{C}_{p,i}(\bar{r},\bar{z},T)C_{o,i}}{C_{o,i}\sum_{j=1}^{m}\left[\bar{Y}_j(\bar{r},\bar{z},T)Y_{e,j} - \frac{\varepsilon_p}{\rho_a}\bar{C}_{p,j}(\bar{r},\bar{z},T)C_{o,j}\right]}$$

$$\cdot \left[\frac{\sum_{k=1}^{m}\left[n_k[\bar{Y}_k(\bar{r},\bar{z},T)Y_{e,k} - \frac{\varepsilon_p}{\rho_a}\bar{C}_{p,j}(\bar{r},\bar{z},T)C_{o,i}]\right]}{n_i K_i}\right]^{n_i} \qquad (1)$$

See Appendix II for the nomenclature which is used in all equations. Equation 1 was used to couple the liquid and solid phase concentrations at both the internal and external adsorbent surfaces.

The DFPSDM, Equations 2-9, describe the fate of an adsorbate, i, within a fixed-bed adsorber. Friedman[10] gives a complete derivation and solution these equations. The liquid-phase mass balance for each adsorbate in dimensionless form is:

$$-\frac{\partial\bar{C}_i(\bar{z},T)}{\partial\bar{z}} + \frac{1}{Pe_i}\frac{\partial^2\bar{C}_i(\bar{z},T)}{\partial\bar{z}^2} = \frac{1}{(Dg_t + 1)}\frac{\partial\bar{C}_i(\bar{z},T)}{\partial T} \qquad (2)$$

$$+ \; 3\,St_i\left[\bar{C}_i(\bar{z},T) - \bar{C}_{p,i}(\bar{r}=1,\bar{z},T)\right]$$

The terms which appear in Eq. 2 account for advective flow, axial dispersion and diffusion, accumulation in the liquid-phase, and transport from the liquid- to solid-phase by liquid-phase mass transfer. The initial condition for Eq. 2 is:

$$\bar{C}_i\ (0 \le \bar{z} \le 1\ ,\ T = 0) = 0 \qquad (3)$$

The boundary conditions for the liquid-phase mass balance are those proposed by Danckwerts (24):

$$1 - \bar{C}_i(\bar{z}=1,T) = \frac{1}{(Dg_t + 1)} \frac{\partial}{\partial T} \left[\int_0^1 \left[\bar{C}_i(\bar{z},T) + 3\, Dg_i \left[\int_0^1 \bar{Y}_i(\bar{r},\bar{z},T)\, \bar{r}^2 d\bar{r} \right] \right] \partial \bar{z} \right] \tag{4}$$

$$\frac{\partial^2 \bar{C}_i(\bar{z}=1,T)}{\partial \bar{z} \partial T} = 0 \quad \text{and} \quad \frac{\partial \bar{C}_i(\bar{z},T=0)}{\partial \bar{z}} = 0 \tag{5}$$

Equations 4 and 5 are derived from equating the mass flux entering and leaving the bed, assuming that transport of the adsorbate into or out of the fixed-bed by axial dispersion and diffusion is negligible when compared to advection. (This is usually referred to as a closed vessel.)

The intraparticle mass balance is expressed by:

$$\frac{1}{\bar{r}^2} \frac{\partial}{\partial \bar{r}} \left[\bar{r}^2 \left[(Ed_{s,i} + D_i\, Ed_{p,i}) \frac{\partial \bar{Y}_i(\bar{r},\bar{z},T)}{\partial \bar{r}} + (Ed_{p,i} - D_i\, Ed_{p,i}) \frac{\partial \bar{C}_{p,i}(\bar{r},\bar{z},T)}{\partial \bar{r}} \right] \right] = \frac{Dg_i}{Dg_t + 1} \frac{\partial \bar{Y}_i(\bar{r},\bar{z},T)}{\partial T} \tag{6}$$

The terms which appears in Eq. 6 account for surface and pore diffusion, and accumulation in the intraparticle-phase, respectively. The initial condition for Eq. 6 is:

$$\bar{Y}_i(0 \le \bar{r} \le 1, 0 \le \bar{z} \le 1, T = 0) = 0 \tag{7}$$

The boundary conditions for Eq. 6 are:

$$\frac{\partial}{\partial \bar{r}} \bar{Y}_i(\bar{r} = 0, 0 \leq \bar{z} \leq 1, T \geq 0) = 0 \qquad (8)$$

$$\frac{Dg_i}{Dg_t + 1} \frac{\partial}{\partial t} \int_0^1 \bar{Y}_i(\bar{r},\bar{z},T)\, \bar{r}^2 d\bar{r} = St_i \left[\bar{C}_i(\bar{z},T) - \bar{C}_{p,i}(\bar{r}=1,\bar{z},T) \right] \qquad (9)$$

Equation 8 results from symmetry. In Eq. 9, the liquid-phase mass flux is equated to the intraparticle-phase mass flux.

Development of Scaling Equations

Six independent dimensionless quantities, $Dg_{s,i}$, $Dg_{p,i}$, $Ed_{s,i}$, $Ed_{p,i}$, Pe_i, and St_i appear in Eqs. 1 - 9. For perfect simulation of a full-scale adsorber each of the six independent dimensionless groups must remain constant as a full-scale adsorber is scaled down to the size of a RSSCT. By setting the dimensionless groups of a small-scale RSSCT adsorber (SC) equal to those of a large-scale column (LC), relationships between key design variables were found.[2]

In order to obtain the scaling relationships, assumptions must be made about changes in phenomena that may affect process performance. Four phenomena that could change with fixed-bed adsorber size are the effects of backwashing, physical characteristics of the GAC, adsorption equilibrium capacity, and adsorption kinetics, thereby, resulting in a poor representation of a full scale adsorber performance by the RSSCT. The impact of backwashing was not considered in developing the scaling equations and is not discussed in this work. However, it may be possible to simulate backwashing in the RSSCT, if the adsorbent particles were distributed in a similar fashion during and after backwashing in the RSSCT and full scale adsorbers.

With respect to equilibrium capacity, exact similarity between the RSSCT

and the full-scale adsorber can be achieved if the isotherm capacity of small GAC used in the RSSCT is identical to the GAC that is used in the full scale adsorber. Adsorption capacity has been shown not to depend on particle size many times in the literature, if adequate equilibration time is given and a representative sample of GAC is used.[14,15,25,26] Berrigan et al.[2,3] demonstrated, that if the GAC preparation procedure which is summarized in the experimental methods section is used to obtain GAC for the RSSCT, then the isotherm capacity for the GAC which is used in RSSCT is identical to that observed in the unground GAC.

With respect to the physical characteristics of the GAC, namely, apparent and bulk density and bed void fraction, Berrigan[1] and Berrigan et al.[2,3] demonstrated that they would have little impact on the performance which would be predicted using the RSSCT for the small differences that were observed.

The final phenomena that could change with process size is adsorption kinetics. The development of proper scaling equations required assumptions of the relationship between adsorbent particle radius and the pore and surface diffusion coefficients, D_s and D_p, respectively. For this study, Dobrzelewski et al.[27] conducted rate studies for trichloroethene (TCE) at concentrations of 10.0 μmol/L, and found that the D_p and D_s value was not significantly dependent on the particle radius. Accordingly, the scaling equations and experimental verification work assume that the surface diffusion coefficients do not depend upon particle size. For the case where there is no change in D_s and D_p with scale-down, perfect similarity may be achieved.

However, in another RSSCT study, Berrigan[1] and Berrigan et al.[3] found that D_s may depend upon particle size and he proposed a method to scale down the RSSCT assuming that the mass transfer rate was controlled by surface diffusion. This procedure was verified experimentally and discussed in detail by Berrigan[1] and Berrigan et al.[2,3] Consequently, the method which is

proposed herein is only valid for the situation where the surface and pore diffusivities of the GAC which is used in the RSSCT is identical to that used in the full-scale plant. This should be verified using several solutes and concentrations of interest, and methods which are described by Hand et al.[28] and Dobrzelewski et al.[27]

By equating the surface diffusivity modulus, $Ed_{s,i}$, and the pore diffusivity modulus, $Ed_{p,i}$ of a small column to that of a full-scale adsorber, the proper relationship between the small column and large column empty bed contact times (EBCTs) may be found.

$$\frac{EBCT_{LC}}{EBCT_{SC}} = \left[\frac{R_{LC}}{R_{SC}}\right]^2 = \frac{t_{LC}}{t_{SC}} \qquad (10)$$

Berrigan[1] and Berrigan et al.[2] provided the details of scaling equation development. The relationship which is defined in Eq. 10 is valid for various combinations of mass transfer resistance controlling the intraparticle resistance: (a) pore diffusion, (b) surface diffusion or (c) both pore and surface diffusion control.

To obtain Eq. 10, the solute distribution parameters, Dg_i, were assumed to be the same for carbons in the small and full scale processes which is valid if these properties are all identical: (a) the equilibrium capacity (b) the bed void fractions, (c) the particle densities and (d) the influent concentrations.

The ratio t_{LC}/t_{SC} is the time which is required to conduct a RSSCT divided by the time it would take to conduct a pilot study. According to Eq. 10, the magnitude of the time savings for the RSSCT is determined by the magnitude of the size reduction of the original GAC in the full-scale system for the RSSCT.

Similarly, in order to have identical Stanton Numbers, St_i, the liquid-phase mass transfer coefficients may be related by the following equation:

$$\frac{k_{f,SC}}{k_{f,LC}} = \frac{R_{LC}}{R_{SC}} \tag{11}$$

In order to satisfy the constraints set forth in Eq. 11, the Sherwood numbers of the small and large columns must be equal for all the adsorbates. Most liquid-phase mass transfer correlations[29] have the following general form:

$$Sh_i = F(Re_i, Sc_i) \tag{12}$$

The correlations of Wilson and Geankopolis[30] and Williamson and Geankopolis[31] have been shown to accurately determine film transfer coefficients in fixed-beds adsorbers.[11,12,14,15,17] Both correlations have the form of Eq. 12. Consequently, the hydraulic loading of the small- and large-scale columns are related to the particle size by this expression:

$$\frac{V_{SC}}{V_{LC}} = \frac{R_{LC}}{R_{SC}} \tag{13}$$

Equation 13 ensures that the Reynolds number of the small-scale process is the same as the large-scale process. Since the Reynolds and Schmidt numbers are identical for the large and small scale columns, Fried[32], Ebach and White[33], and Miyauchi and Kikuchi[34] have shown that Peclet numbers which are based on particle size, Pe_d, will be identical. Furthermore, the column length to particle size ratios, L/R, for the small- and large-scale columns are equal. This implies that the small- and large- scale column have equal Peclet numbers which are based on column length (Pe_L). Consequently, Eq. 13 guarantees exact similarity whether plug flow or dispersed flow conditions exist.

RESULTS AND DISCUSSION

Theoretical Verification of the Scaling Procedure Using Mathematical Model Calculations

Friedman[10] demonstrated that pore diffusion was unimportant for the column conditions similar to those reported in Tables 1 and 2; consequently, to illustrate the applicability of the scaling procedure, the DFHSDM was used to predict the multicomponent effluent concentration history profiles of the large-scale adsorber and the RSSCT which was designed to simulate full-scale performance. The computer algorithms are described by Friedman.[10] The design and operational parameters are given in Table 1. The influent contained cis-dichloroethylene (DCE), trichloroethene (TCE), tetrachloroethene (PCE), toluene, and xylene at concentrations near those measured in a related field study.[1,2] The chemical, mass transfer and dimensionless parameters for these adsorbates are shown in Table 2. The surface diffusivities for components other than TCE were calculated using the correlation developed by Dobrzelewski et al.[27] The RSSCT and large-scale dimensionless parameters are identical; consequently, only one set is given for each adsorbate. As shown in Figure 1, the breakthrough profiles for the RSSCT and large scale breakthrough profiles of the RSSCT and large scale adsorber are identical for each component in Table 1. Therefore, in theory, the RSSCT can be conducted in 1.05% of the time required for a pilot-scale adsorber, regardless of the adsorbate mixture, if the GAC particle radius is reduced from 0.0513 cm to 0.00525 cm and the surface diffusivity is identical for the small and large GAC particle sizes.

Experimental Verification of the Scaling Equations

The scaling procedure was verified by comparing performances of a pilot-scale adsorber to a RSSCT with US No. 60X80 mesh size GAC. The design and operational parameters are listed in Table 3. This six component mixture in order of decreasing adsorptability was used to test the predictive ability of

the RSSCT: chloroform, chlorodibromomethane, 1,2-dibromoethane, bromoform, trichloroethene, and tetrachloroethene. The influent and effluent concentration concentrations for three of the six components for the pilot-scale adsorber and the RSSCT are plotted in Figure 2-4. As shown in Figures 2-4, the influent concentration of the RSSCT was more consistent than that of the pilot plant because the pilot plant influent was made by mixing a concentrated feed with dilution water and the influent for the RSSCT was made-up in one batch. The pilot-scale adsorber study which required 818 liters of water for 3.47 days of operation was only conducted for 5000 bed volumes of treatment because mechanical failure forced the end of operation. However, in 24 hours, the small-scale adsorber had treated 33,000 bed volumes using only 60 liters of water. As shown in Figures 2-4, the agreement between the pilot scale adsorber and RSSCT effluent concentration profiles was good. The agreement for the other three components which were not shown was just as good.[23] The slight discrepancies that appear between breakthrough profiles for the pilot-scale adsorber and the RSSCT appear to correspond with differences in the influent concentrations which are plotted in Figures 2-4 and summarized in Table 3. Consequently, an RSSCT which is conducted with 60X80 mesh GAC can be conducted in 4.2% of the time that the pilot-scale column can be conducted.

CONCLUSIONS

Rapid small-scale fixed bed adsorption tests (RSSCT) may predict full-scale adsorber performance in less time and at less expense than a pilot study by plotting the effluent concentration history in terms of the bed volumes fed. RSSCTs use a smaller size granular activated carbon (GAC) that is prepared from the GAC which is to be used in the full scale process.

Several RSSCTs may be used to rapidly evaluate several empty bed contact times of important process configurations such as beds-in-series or in-parallel. In order to select the least expensive adsorber operation, both the

fixed-bed adsorber configuration and EBCT have to be selected. In the design of pulsed-beds or beds in-series, the EBCT of the MTZ needs to be determined. Following the procedure which is discussed by Hand et al.[35] and Crittenden and Hand,[36] one could use the breakthrough profiles of the RSSCT to estimate the EBCT of the MTZ of the large adsorber for a single component, if constant pattern exists. Lee et al.[26] and Crittenden and Hand[36] have discussed the proper selection of the adsorber design variables. Accordingly, the RSSCT should be configured to assess the performance of fixed-bed operations.

Like pilot studies, the RSSCT will match full-scale performance only if the granular activated carbon (GAC) used in the full-scale adsorber has the same equilibrium capacity, and bulk density as that used in the RSSCT. Also like pilot studies, the RSSCT can simulate the full-scale system only if the operating temperatures and the influent concentrations are the same.

Scaling equations were derived from dimensionless groups which appeared in the dispersed-flow, pore- surface- diffusion model. The choice of a reduced size carbon determines the the proper hydraulic loading rate and empty bed contact time for the RSSCT. Perfect similarity between RSSCT and full-scale adsorber may be achieved if the surface diffusivity for a representative influent solute on the RSSCT GAC is the same as that on the full-scale GAC. This must be demonstrated for similar compounds and concentrations because in another study Berrigan et al.[2,3] discovered that there appeared to be a difference the surface diffusivities in the GACs that were used in the full scale adsorber and RSSCT. In addition, Berrigan[2,3] developed scaling equations for that case.

A batch rate study should be conducted according to Hand et al.[28] and the easier way to decide whether the surface diffusivities for the full-scale and RSSCT GACs are identical is to plot concentration versus t/R^2. The profiles

for both GACs should be identical when they are plotted in this manner if their intraparticle diffusivities are identical.

The following equations are all that is needed for the design of an RSSCT if surface diffusivities are the same:

$$\frac{EBCT_{LC}}{EBCT_{SC}} = \left[\frac{R_{LC}}{R_{SC}}\right] = \frac{t_{LC}}{t_{SC}} \qquad (10)$$

$$\frac{V_{SC}}{V_{LC}} = \frac{R_{LC}}{R_{SC}} \qquad (13)$$

Model calculations were made with the dispersed-flow homogeneous surface-diffusion model (DFHSDM) gave identical breakthrough profiles for a RSSCT and full-scale adsorber that were treating a five component mixture. Therefore, in theory, the RSSCT can be conducted in 1.05% of the time required for a pilot-scale adsorber, regardless of the adsorbate mixture, if the GAC particle radius is reduced from 0.0513 cm to 0.00525 cm and the surface diffusivity is identical for the small and large GAC particle sizes.

Measurement of the trichloroethene surface diffusivities in GACs which were to be used in the pilot-scale and RSSCT studies indicated that it was possible to design an RSSCT to perfectly simulate the performance of a larger adsorber. Accordingly a laboratory verification of the RSSCT was conducted and agreement between the laboratory pilot-scale adsorbers and the RSSCT breakthrough profiles was good. The RSSCT which was conducted with U.S. No. 60X80 mesh (.0105cm) GAC was conducted in 4.2% of the time that the pilot-scale column was conducted.

Before this method is considered generally applicable, more field testing is required[2,3] because it appears that it may be possible to prepare a smaller mesh GAC for use in a RSSCT that will give identical results as a pilot test.

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APPENDIX II. NOMENCLATURE

Roman Letters

$Bi_{s,i}$	Biot number based on surface diffusivity (dimensionless); $Rk_{f,i}(1-\varepsilon)/(D_{s,i}\ Dg_{s,i}\ \varepsilon)$
BVF	bed volumes of feed (dimensionless)
BVF_{max}	maximum number of bed volumes that can be treated (dimensionless)
$\bar{C}_i(\bar{z},T)$	reduced adsorbate concentration in bulk phase as a function of dimensionless axial position and dimensionless time (dimensionless); $C_i(z,t)/C_{o,i}$
$C_{o,i}$	initial bulk phase concentration (M/L^3)
$\bar{C}_{p,i}(\bar{r},\bar{z},T)$	reduced adsorbate concentration in adsorbent pores as a function of dimensionless radial and axial position and dimensionless time (dimensionless); $C_{p,i}(r,z,t)/C_{o,i}$
CSA	cross-sectional area of adsorber
De_i	axial dispersivity based on adsorber length and interstitial velocity (L^2/t)
Dg_i	combined solute distribution parameter (dimensionless); $(Dg_{s,i} + Dg_{p,i})$
$Dg_{p,i}$	pore solute distribution parameter (dimensionless); $\varepsilon_p(1-\varepsilon)/\varepsilon$
$Dg_{s,i}$	surface solute distribution parameter (dimensionless); $\rho_a q_{e,i}(1-\varepsilon)/\varepsilon C_{o,i}$
Dg_t	total solute distribution parameter (dimensionless); $(Dg_{p,i} + Dg_{s,i})$ over all all components
D_i	ratio of surface to pore diffusion transport (dimensionless); $(Ed_{s,i}Dg_{p,i})/(Ed_{p,i}Dg_{s,i})$
D_L	free liquid diffusivity (L^2/t)
$D_{p,i}$	pore diffusivity based on pore void fraction (L^2/t)
$D_{s,i}$	surface diffusivity (L^2/t)
Dia	column diameter (L)
EBCT	τ/ε, V_B/Q or L/V_s, fluid residence time in the bed which is devoid of the adsorbent or empty bed contact time (t)
$EBCT_{min}$	minimum empty bed contact time required for constant pattern (t)

$EBCT_{mtz}$	empty bed contact time of the mass transfer zone (t)
$Ed_{p,i}$	pore diffusion modulus (dimensionless); $D_{p,i}Dg_{p,i}\tau/R^2$
$Ed_{s,i}$	surface diffusion modulus (dimensionless); $D_{s,i}Dg_{s,i}\tau/R^2$
i	subscript denoting a solute i
K_i	Freundlich isotherm capacity constant $(M/M)(L^3/M)^{1/n}$
$k_{f,i}$	film transfer coefficient (L/t)
$1/n_i$	Freundlich isotherm intensity constant (dimensionless)
L	length of fixed-bed (L)
L_{min}	minimum adsorber length to establish a constant pattern (L)
L_{mtz}	length of the mass transfer zone (L)
Pe_i	Peclet number based on interstitial velocity and adsorber length (dimensionless); Lv/De_i
$Pe_{i,D}$	$2vR/D_e$, Peclet number based on particle diameter (dimensionless)
$Pe_{i,mtz}$	vL_{mtz}/D_e, Peclet number based on length of the mass transfer zone (dimensionless)
$q_{e,i}$	adsorbent phase concentration in equilibrium with initial bulk phase concentration (M/M); $K_i C_{o,i}^{1/n_i}$
$\bar{q}_i(\bar{r},\bar{z},T)$	reduced adsorbent phase concentration as a function of dimensionless radial and axial position and dimensionless time (dimensionless); $q_i(r,z,t)/q_{e,i}$
Q	fluid flow rate (L^3/t)
r	radial coordinate (L)
$\bar{r}$	reduced radial coordinate (dimensionless); r/R
R	adsorbent radius (L)
Re	Reynolds number (dimensionless)
Sc	Schmidt number (dimensionless)
Sh_i	$k_{fi}2R/D_L$, Sherwood number, (dimensionless)
St_i	modified Stanton number (dimensionless); $k_{f,i}\tau(1-\varepsilon)/R\varepsilon$
$St_{i,min}$	minimum Stanton number required to establish constant pattern (dimensionless)

t	elapsed time (t)
$t_{i,min}$	elapsed time corresponding to the minimum EBCT required to establish constant pattern conditions (t)
$\bar{T}$	reduced time (mass Throughput) (dimensionless); $t/\tau(Dg_t + 1)$ (used in fixed-bed models)
v	interstitial velocity (L/t); v_s/ε
v_s	superficial velocity (L/t)
V_b	molal volume at the normal boiling point (L^3/M)
V_B	volume of the bed (L^3)
V_p	pore volume per mass of adsorbent (L^3/M)
$Y_{e,i}$	total adsorbent phase concentration in equilibrium with initial bulk phase concentration (M/M); $q_e + \varepsilon_p C_{io}/\rho_a$
$Y_i(r,t)$	total adsorbent phase concentration as a function of radial position and time (M/M); $q_i(r,t) + [\varepsilon_p C_{p,i}(r,t)/\rho_a]$
$Y_i(r,z,t)$	total adsorbent phase concentration as a function of radial and axial position and time (M/M); $q_i(r,z,t) + [\varepsilon_p C_{p,i}(r,z,t)/\rho_a]$
$\bar{Y}_i(\bar{r},\bar{z},T)$	reduced total adsorbent phase concentration as a function of dimensionless radial and axial position and dimensionless time (dimensionless); $Y_i(r,z,t)/Y_{e,i}$
z	axial coordinate (L)
$\bar{z}$	reduced axial coordinate (dimensionless); z/L

Greek Letters

ε	fraction of volumetric space in reactor unoccupied by adsorbent, or void fraction (dimensionless)
ε_p	fraction of volumetric space in adsorbent phase unoccupied by adsorbent on the pore volume fraction (dimensionless)
ρ_a	adsorbent density which includes pore volume (M/L^3)
ρ_b	adsorbent bulk density (M/L^3)
ρ_L	density of water (M/L^3)
τ	fluid residence time in packed bed, or packed bed contact

	time (t)
τ_p	tortuosity of adsorbent (dimensionless)
μ	viscosity of water (M/Lt)

Acronyms

DCE = cis-dichloroethene

DFPSDM = dispersed-flow pore- surface- diffusion model

GAC = granular activated carbon

LC = large scale

PCE = tetrachloroethene

PFHSDM = plug flow homogeneous solid diffusion model

RSSCT = rapid small scale adsorber test

SC = small scale or RSSCT

TCE = trichloroethene

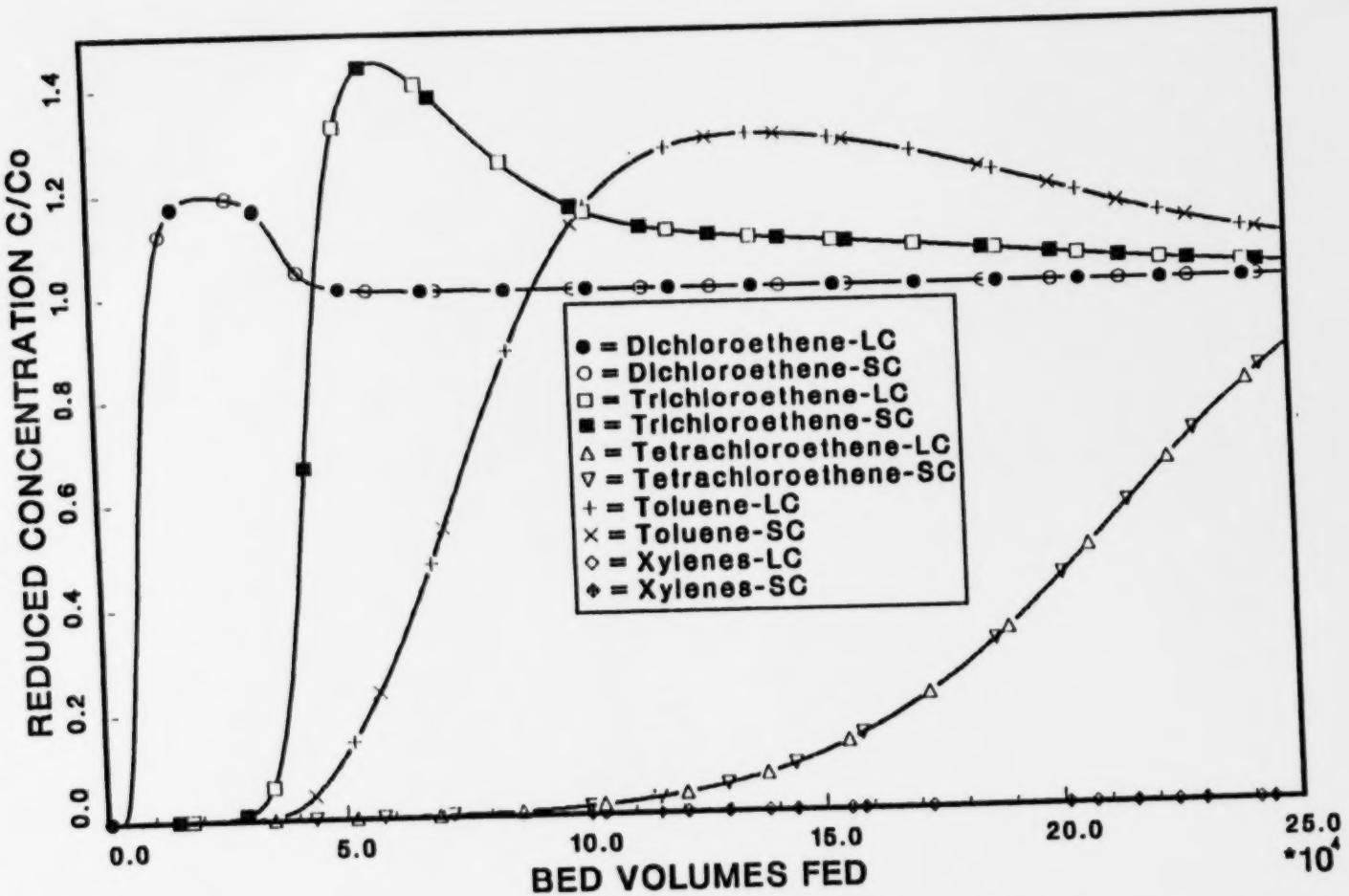

Figure 1. Comparison of DFHSDM model predictions of full-scale adsorber breakthrough profiles for dichloroethene, trichloroethene, tetrachloroethene, toluene, and xylenes to the DFHSDM predictions for a small-column test assuming constant surface diffusivity. Column parameters are found in Tables 1 and 2.

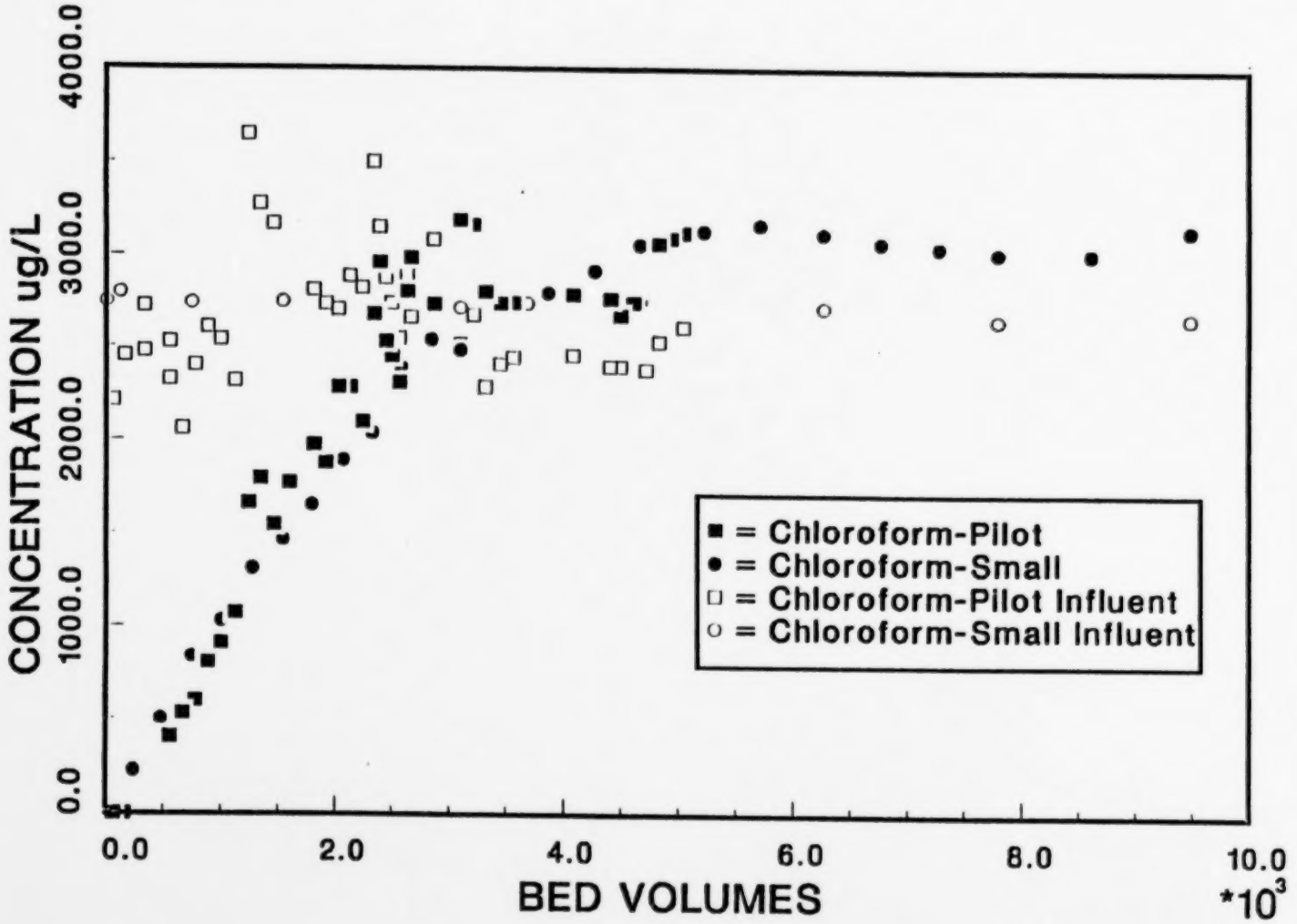

Figure 2. Comparison of the chloroform breakthrough profiles for the RSSCT and pilot-scale columns. Influent data are shown. Operating parameters are presented in Table 3.

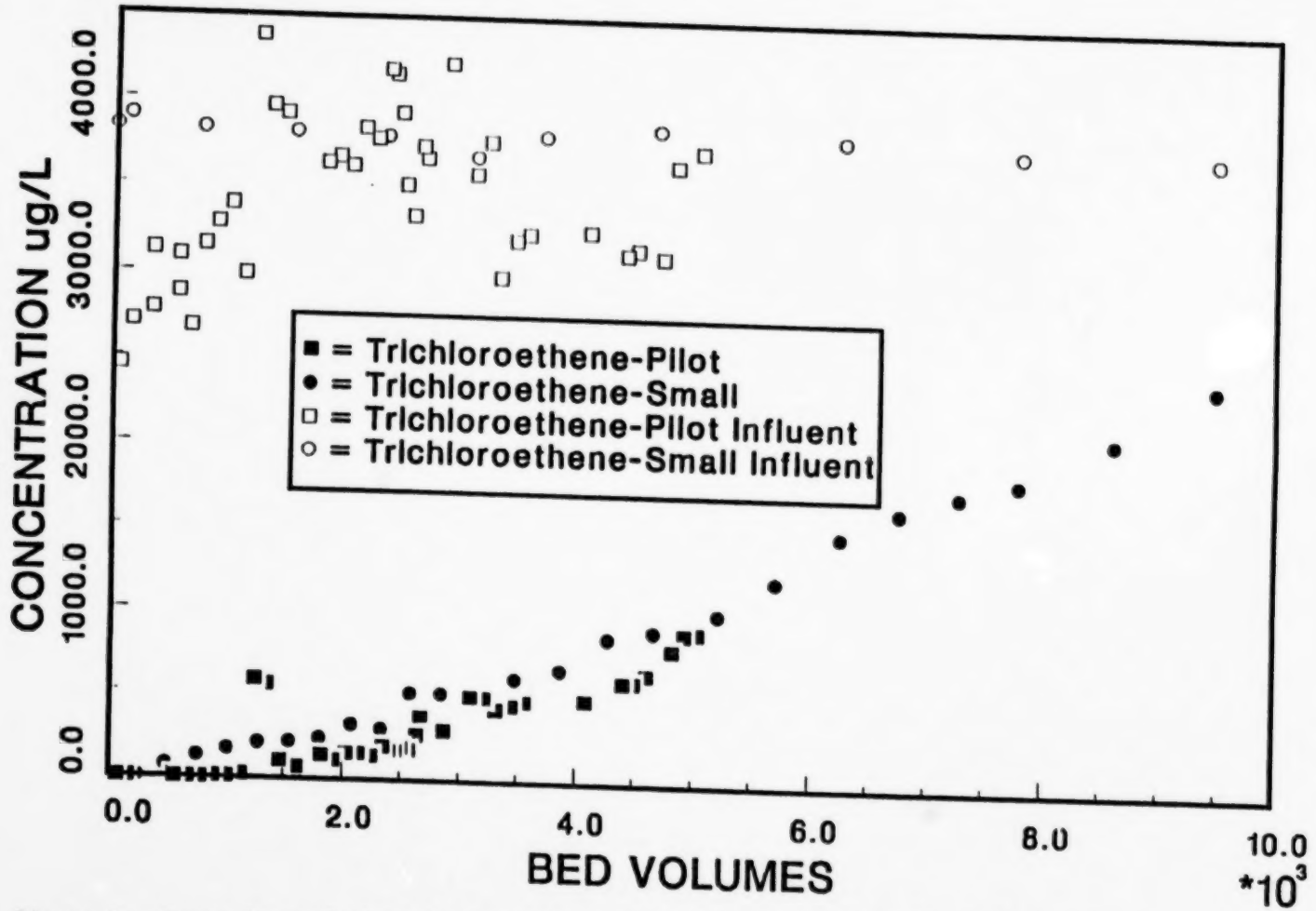

Figure 3. Comparison of the trichloroethene breakthrough profiles for the RSSCT and pilot-scale columns. Influent data are shown. Operating parameters are presented in Table 3.

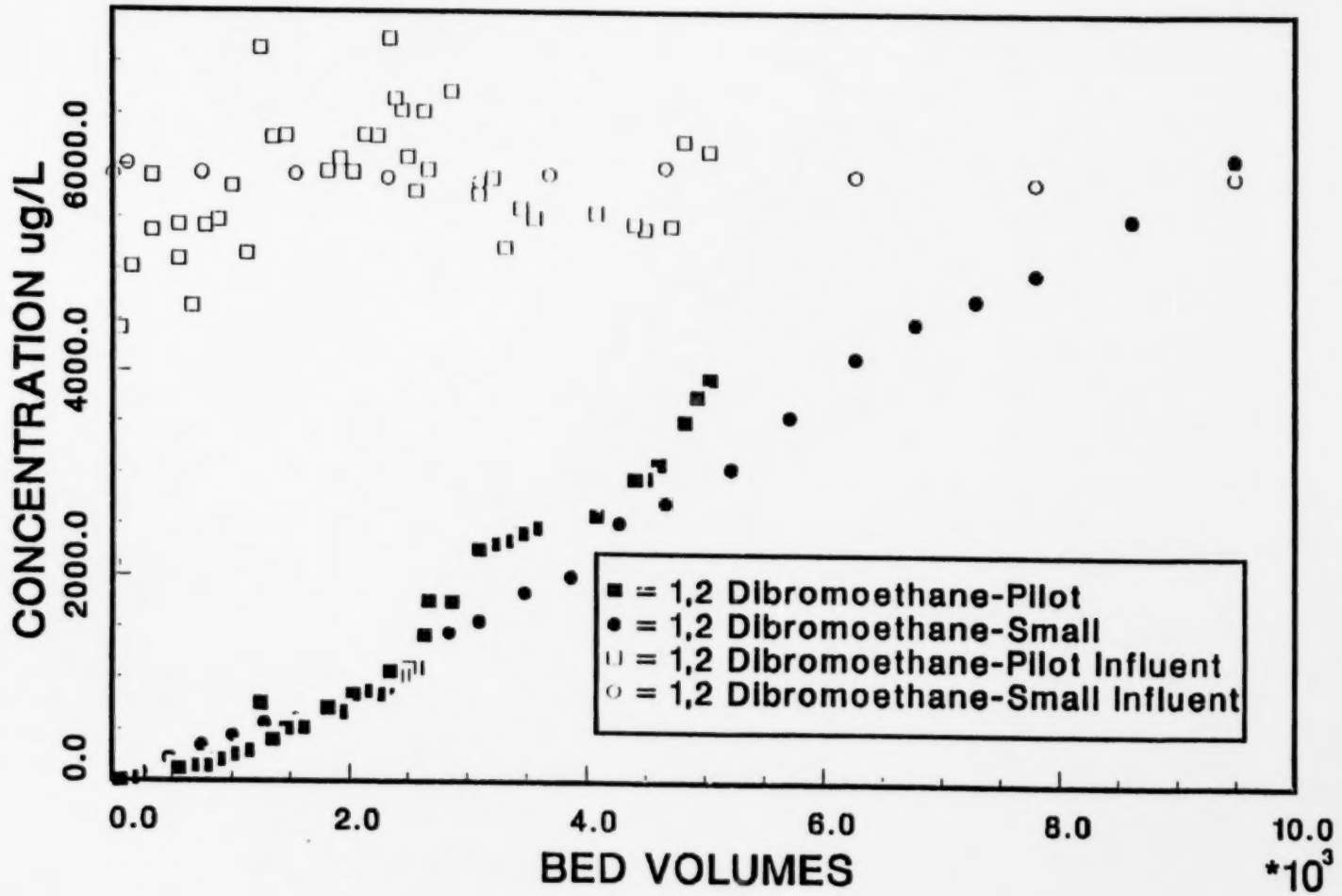

Figure 4. Comparison of the 1,2 dibromoethane breakthrough profiles for the RSSCT and pilot-scale columns. Influent data are shown. Operating parameters are presented in Table 3.

Table 1. Comparison of design and operational parameters of a full-scale column and a rapid small-scale column test which is designed to simulate full-scale performance.

		Full Scale Adsorber	RSSCT
GAC Packing Characteristics			
ρ_a	kg/m^3	803.4	803.4
ε		0.40	0.40
R	m	5.13×10^{-4}	5.25×10^{-5}
Column and Flow Specifications			
Column Diameter	m	2.44	0.00525
Column Length	m	0.417	0.0426
EBCT	s	300	3.14
Cross-Sectional Area	m^2	4.67	2.16×10^{-5}
v_s	m/hr	5.00	48.9
Bed Volume	m^3	1.946	9.23×10^{-7}
Flow rate	L/s	6.483	2.93×10^{-4}
Required Volume to Simulate 72,800 Bed Volumes of Feed	m^3	1.42×10^5	.0672
Run time to Simulate 72,800 Bed Volumes of Feed	days	252	2.65
Head loss	N/m^2	591	56,400
	PSI	0.10	8.18

Table 2. Chemical and dimensionless parameters for a full-scale column and a RSSCT for (a) cis-dichloroethylene (DCE), (b) trichloroethylene (TCE), (c) tetrachloroethylene (PEC), (d) toluene, and (e) xylene. The column parameters may be found in Table 1 under the headings of full-scale adsorber and RSSCT which is designed to simulate the full-scale adsorber.

q	DCE (a)	TCE (b)	PCE (c)	Toluene (d)	Xylene (e)
C_o μmol/L	0.413	1.52	0.9045	1.042	0.474
K μmol/g(L/μmol)$^{1/n}$	39.0*	196.6*	650.0**	300.0**	1500.0**
1/n	0.7045	0.4163	0.4579	0.4400	0.3500
D_s m^2/s	7.17×10^{-14}	3.75×10^{-14}	7.41×10^{-15}	2.36×10^{-14}	6.28×10^{-15}
D_e m^2/s	9.81×10^{-6}	9.93×10^{-6}	1.028×10^{-7}	1.033×10^{-7}	10.52×10^{-7}
k_f full-scale m/s	2.19×10^{-3}	2.03×10^{-3}	1.91×10^{-3}	1.89×10^{-3}	1.79×10^{-3}
k_f RSSCT m/s	2.14×10^{-2}	1.98×10^{-2}	1.87×10^{-2}	$1.85 \times^{10-2}$	1.74×10^{-2}
Pe	147.0	145.2	140.3	139.7	137.2
St	7.69	7.12	6.71	6.64	6.28
Bi	8.46	2.50	2.67	1.94	0.831
E_d	0.908	2.85	2.51	3.42	7.56

Column parameters may be found in Table 1 under the headings of full scale adsorber and RSSCT which is designed to simulate full scale performance, RSSCT.

* Measured by Luft (16) and Crittenden (23).
** Determined from Dobbs and Cohen (37).

Table 3. Pilot-Scale and Small-Scale Design Parameters.

GAC Packing Characteristics:		Large Column	RSSCT
ρ_b	kg/m^3	478	482
ε		0.40	0.40
R	cm	$5.13X10^{-4}$	$1.05X10^{-4}$
Flow Specifications:			
Column Diameter	m	0.050	0.011
Column Length	m	0.0833	0.0171
EBCT	s	60	2.51
CSA	m^2	$1.96X10^{-2}$	$9.50X10^{-3}$
V_s	m/hr	5.00	24.4
Bed Volume	L	0.164	$1.62X10^{-3}$
Flow rate	L/min	0.164	0.0387
Required Volume to Simulate 16,000 Bed Volumes of Feed	L	2618	25.9
Run time to Simulate 16,000 Bed Volumes of Feed	days	11.1	0.466
Head loss	N/m^2	118	3220
	PSI	0.02	0.47
Average Influent Concentrations µg/L:			
Chloroform		2609	2670
Trichloroethene		3397	3763
Chlorodibromomethane		5367	5293
1,2 Dibromoethane		5730	5845
Bromoform		4366	4731
Tetrachloroethane		2281	3018
Influent Temperature	°C	11±1	11±1